Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Magnetism and Magnetic Materials 270 (2004) 305–311

Journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

The order of magnetic phase transition in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ compounds

Xu Bo Liu, D.H. Ryan, Z. Altounian*

Department of Physics, Center for the Physics of Materials, McGill University, Rutherford Physics Building, 3600 University Street, Montreal, Que., Canada H3A 2T8

Received 6 June 2003; received in revised form 21 August 2003

Abstract

Magnetic transitions in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ compounds with $x = 0$–0.08, have been studied by DC magnetic measurements and Mössbauer spectroscopy. The temperature dependence of the Landau coefficients has been derived by fitting the magnetization, $M(\mu_0 H)$, using the Landau expansion of the magnetic free energy. For $x \leqslant 0.02$ there is a strongly first-order magnetic phase transition between ferromagnetic and paramagnetic (F–P) states in zero external field and a metamagnetic transition from paramagnetic to ferromagnetic (P–F) above T_c. Increasing the cobalt content drives the F–P transition towards second order and eliminates the metamagnetic transition.

PACS: 75.30.Kz; 76.80.+y; 75.30.Sg

Keywords: Magnetic transition; Landau coefficients; Mössbauer; Rare earth

1. Introduction

Since the discovery of the giant magnetocaloric effect (MCE) in $Gd_5Si_2Ge_2$ ($\Delta S = 18.5$ J/kg K under 5 T field at $T_c = 276$ K) [1], research interest in magnetocaloric materials that can be used near room temperature has increased considerably. Recently, it was reported that the $NaZn_{13}$-type compounds $LaFe_{11.4}Si_{1.6}$ and $LaFe_{11.2}Co_{0.7}Si_{1.1}$ exhibit large magnetic entropy changes near their Curie temperatures, T_c, ($\Delta S = 19.4$ J/kg K at $T_c = 208$ K and $\Delta S = 20.3$ J/kg K at $T_c = 274$ K, respectively, in a 5 T field) [2,3]. Fujita et al [4] found that $La(Fe_xSi_{1-x})_{13}$ compounds with $x = 0.86$ and 0.88 exhibit a first-order magnetic transition at T_c as well as an itinerant electron metamagnetic transition (IEM) above T_c. It is believed that the large entropy change in $LaFe_{11.4}Si_{1.6}$ is also related to the presence of a first-order magnetic transition near T_c [2].

An ideal magnetic refrigerant should work over a wide range of temperatures (e.g. 220–330 K) and would therefore likely be a composite of several magnetocaloric materials with different Curie temperatures. The replacement of Fe by Co in $LaFe_{11.4}Si_{1.6}$ can increase T_c but leads to a decrease in maximum magnetic entropy. This

*Corresponding author. Tel.: +1-514-398-1635; fax: +1-514-398-6526.

E-mail addresses: liux@physics.mcgill.ca (X.B. Liu), zaven@physics.mcgill.ca (Z. Altounian).

0304-8853/$ - see front matter
doi:10.1016/j.jmmm.2003.08.028

appears to be related to preferential substitution of Co for Fe in these compounds and to a change in the order of the ferromagnetic to paramagnetic (F–P) transition near T_c [5]. In this work, we investigate the nature of the magnetic phase transitions in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ alloys using DC magnetization measurements and Mössbauer spectroscopy.

2. Experimental techniques

Compounds with nominal composition $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ ($x = 0$, 0.02, 0.04, 0.06, 0.08) were prepared by tri-arc melting in a purified Ar atmosphere. The ingots were annealed at 1273 K for 15 days in evacuated quartz tubes. The results of X-ray diffraction analysis indicated that the materials were single phase $NaZn_{13}$ cubic structures for all compounds. However, Mössbauer spectra clearly show the presence of a small amount ($\leqslant 4$ at.%) of α-Fe in the samples with $x =$ 0, 0.04, 0.06. The absence of α-Fe from the X-ray diffraction patterns indicates that the impurity is probably present as a nano-crystalline grain-boundary phase. Curie temperatures, T_c^{χ}, were determined by ac-susceptibility (χ_{ac}), using a quantum design physical property measurement system (PPMS) magnetometer. The magnetometer (PPMS) was also used for DC-magnetization measurements in fields of up to 9 T.

The Mössbauer spectra for $La(Fe_{1-x}Co_x)_{11.4}$-$Si_{1.6}$ samples were obtained in a standard transmission geometry with a 1 GBq ^{57}Co**Rh** source on a constant acceleration spectrometer, which was calibrated against an α-iron foil at room temperature. A liquid nitrogen flow cryostat was used to obtain temperatures between 100 and 300 K. Spectra were fitted using a standard nonlinear least-squares minimization method.

3. Results and discussion

3.1. Magnetic behavior near T_c

The magnetic free energy, $F(M,T)$, generally can be expressed as a Landau expansion in the magnetization M [6]:

$$F(M,T) = \frac{a_1(T)}{2}M^2 + \frac{a_3(T)}{4}M^4 + \frac{a_5(T)}{6}M^6 + \cdots - \mu_0 HM \quad (1)$$

and the temperature and magnetic field dependence of $F(M,T)$ determines the nature of the magnetic transition. The Landau coefficients are accessible through the equation of state linking M and the magnetic field, $\mu_0 H$ [6]:

$$\mu_0 H = a_1(T)M + a_3(T)M^3 + a_5(T)M^5. \quad (2)$$

The temperature dependence of the leading order Landau coefficients $a_1(T)$ and $a_3(T)$ allows us to identify two characteristic temperatures and thereby distinguish first- and second-order magnetic transitions. The susceptibility must be positive and exhibits a maximum at T_c, therefore the (positive) minimum in $a_1(T)$ marks $T_c^{a_1}$. $a_3(T)$ crosses zero at a second temperature, T_0. If $T_0 = T_c$, then the transition is second order, while $T_0 > T_c$ implies a first-order transition.

In order to understand the nature of the magnetic transitions in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ alloys, the magnetization, $M(H)$, was measured as a function of temperature and external field. Compounds of $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ are magnetically soft with coercivities ($\mu_0 H_{ci}$) less than 5 mT, allowing the demagnetization factor to be determined from the initial slope of magnetization curves measured below T_c. All magnetization data presented here have been corrected using a demagnetizing factor of about 0.16.

The Landau coefficients $a_1(T)$, $a_3(T)$ and $a_5(T)$ were determined by fitting the magnetic field, $\mu_0 H$ against magnetization, $M(\mu_0 H)$, using Eq. (2). As an example, Fig. 1 shows magnetization data for $La(Fe_{0.96}Co_{0.04})_{11.4}Si_{1.6}$ at different temperatures together with the fitted curves. The temperature dependence of the Landau coefficients derived from these fits is shown in Fig. 2 for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ with $x = 0$ and 0.06. As expected, $a_1(T)$ for each of the alloys is positive with a minimum at T_c, corresponding to a maximum in the susceptibility, χ. Similarly, $a_3(T)$ increases from negative to positive, crossing zero at T_0. The value of $a_3(T)$ at T_c is negative for

$LaFe_{11.4}Si_{1.6}$, but zero for $La(Fe_{0.94}Co_{0.06})_{11.4}Si_{1.6}$, indicating that the zero external field magnetic transitions at T_c are first- and second-order, respectively, [6–8]. Table 1 shows the characteristic temperatures derived from this Landau analysis for the alloys with $x=0$, 0.02, 0.04, 0.06 and 0.08. Also shown are transition temperatures derived from χ_{ac} and Mössbauer data.

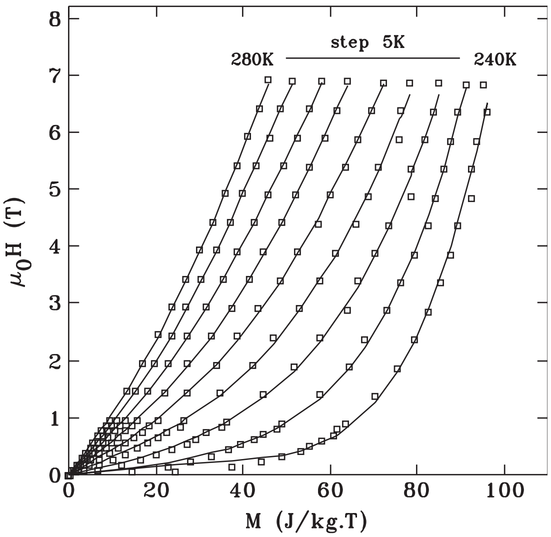


Fig. 1. Magnetization, $M(\mu_0 H)$ of $La(Fe_{0.96}Co_{0.04})_{11.4}Si_{1.6}$ at different temperatures. The solid lines represent the fits to Eq. (2).

The composition dependence of $T_c^{a_1}$ and T_0 (Fig. 3) shows that the replacement of Fe by Co in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ changes the magnetic transition from first to second order. Both transition temperatures increase monotonically, however, T_0 is larger than T_c for the alloys with $x \leqslant 0.02$, indicating a first-order magnetic transition at T_c. For the alloys with $x \geqslant 0.06$, T_0 is equal to T_c, indicating that the magnetic transition at T_c is now second order. For $x = 0.04$, T_0 appears to the same as T_c, but Mössbauer results shown below suggest that the magnetic transition at T_c is weakly first order.

Arrott plots for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ at temperatures about 10 K above T_c are shown in Fig. 4. The curves have negative slopes or inflection points above T_c for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ with $x \leqslant 0.02$, indicating a metamagnetic transition from a paramagnetic to a ferromagnetic state [9]. However, for $x \geqslant 0.04$, the Arrott curves have positive slopes and no inflection points, in agreement with a positive $a_3(T)$ for $T > T_c$. Thus the addition of Co weakens or eliminates the metamagnetic transition in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ alloys.

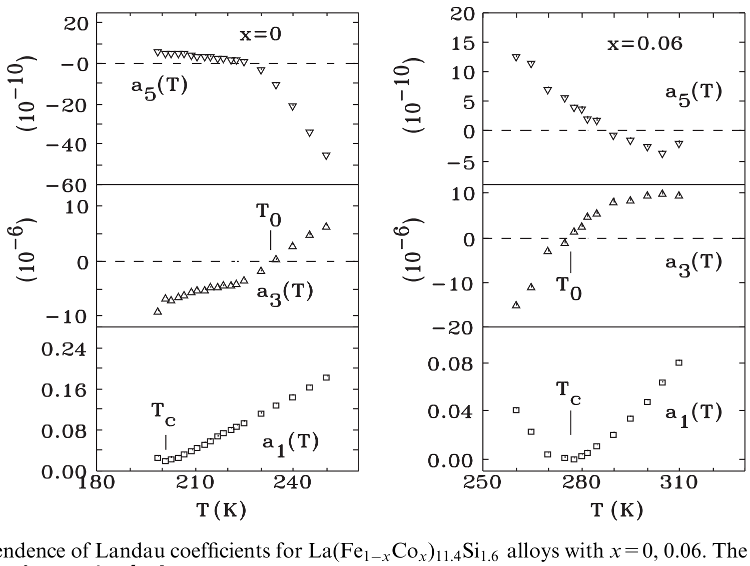


Fig. 2. Temperature dependence of Landau coefficients for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ alloys with $x=0$, 0.06. The units for $a_1(T)$, $a_3(T)$ and $a_5(T)$ are T^2 kg/J, T^4 kg^3/J^3 and T^6 kg^5/J^5, respectively. Error bars are smaller then the points.

Table 1
Characteristic temperatures for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ compounds

x	T_c^{χ} (K) (Susceptibility)	$T_c^{B_{hf}}$ (K) (Mössbauer)	T_c^{Br} (K) (Brillouin)	$T_c^{a_1}$ ($a_1(T)=\min$)	T_0 (K) ($a_3(T)-0$)
0	203 ± 1	202 ± 3	249 ± 5	202 ± 3	233 ± 3
0.02	228 ± 1			227 ± 3	241 ± 3
0.04	257 ± 1	254 ± 3	270 ± 3	255 ± 3	255 ± 3
0.06	279 ± 1	281 ± 3	281 ± 3	279 ± 3	279 ± 3
0.08	300 ± 1			300 ± 3	300 ± 3

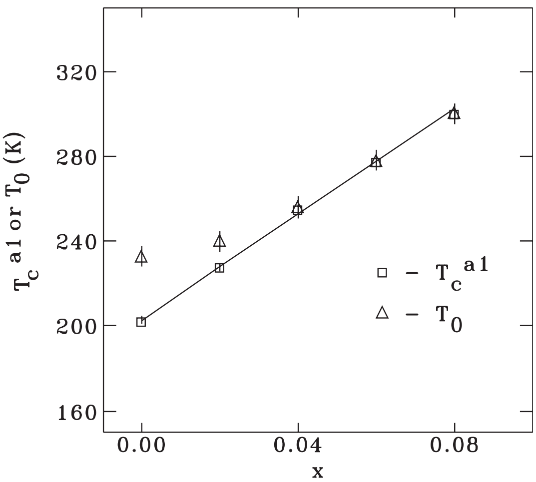


Fig. 3. The variation of Curie temperature, $T_c^{a_1}$, and T_0 with Co content for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$, derived from the temperature dependences of $a_1(T)$ and $a_3(T)$ (see text).

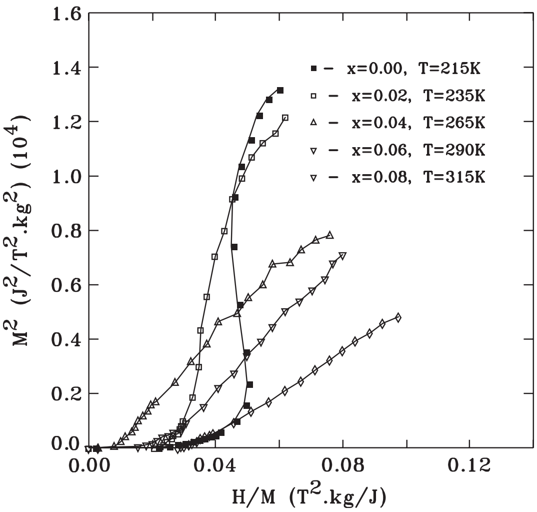


Fig. 4. Arrott plots for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ alloys at a temperature of about 10 K above T_c.

The strongly first-order magnetic transition at T_c and the field induced paramagnetic to ferromagnetic metamagnetic transition above T_c are the main reasons that the alloys with $x\leqslant0.02$ have much higher magnetic entropy changes than those with $x\geqslant0.04$.

3.2. ^{57}Fe Mössbauer results

In order to gain more insight into the nature of the magnetic transition in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ alloys, Mössbauer spectra were obtained at different temperatures. The temperature dependence of ^{57}Fe Mössbauer spectra for La $(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ with $x=0$, 0.04 and 0.06 are shown in Figs. 5(a) 6(a) 7(a), respectively. The spectrum for each compound has a very small subspectrum corresponding to α-Fe (less than 4 at. %).

In Fig. 5(a), the spectrum for $LaFe_{11.4}Si_{1.6}$ is dominated by a Gaussian-broadened magnetic sextet at temperatures, $T\leqslant200$ K. With increasing temperature, the average hyperfine field, $B_{hf}(T)$, of the sextet decreases slowly. However, an asymmetric paramagnetic doublet develops around 205 K and co-exists with the magnetic sextet which retains a significant hyperfine field. This coexistence of the magnetic and paramagnetic components is due to thermal hysteresis and is an indication of a first-order transition. By 215 K, the sextet is totally replaced by the doublet and the compound is paramagnetic. By contrast, spectra for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ with $x=0.04$ and 0.06

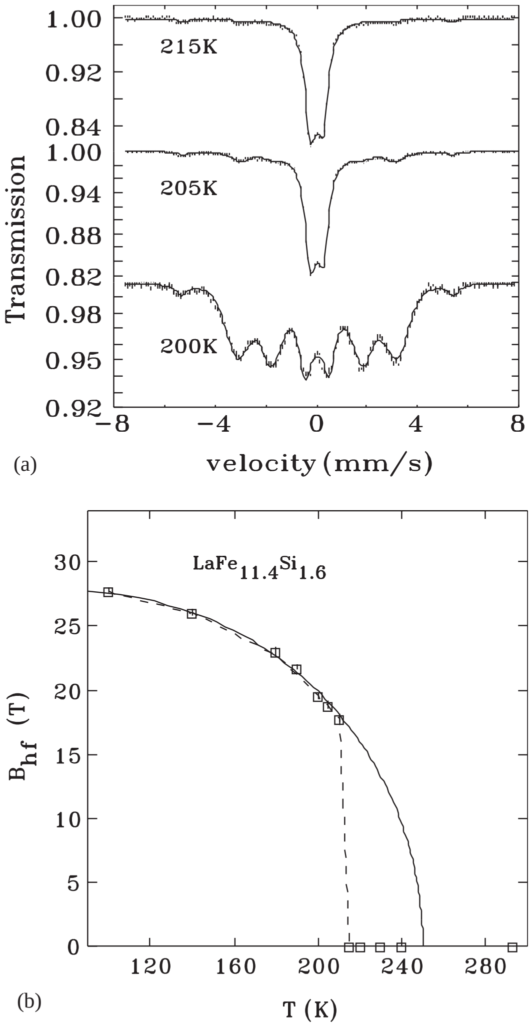


Fig. 5. (a) [57]Mössbauer spectra of $LaFe_{11.4}Si_{1.6}$ at several temperatures. The solid lines are least-squares fits to the Mössbauer spectra; (b) temperature dependence of the average hyperfine magnetic field. The solid line is calculated using Brillouin function. The dashed line through the experimental data points is a guide to the eye.

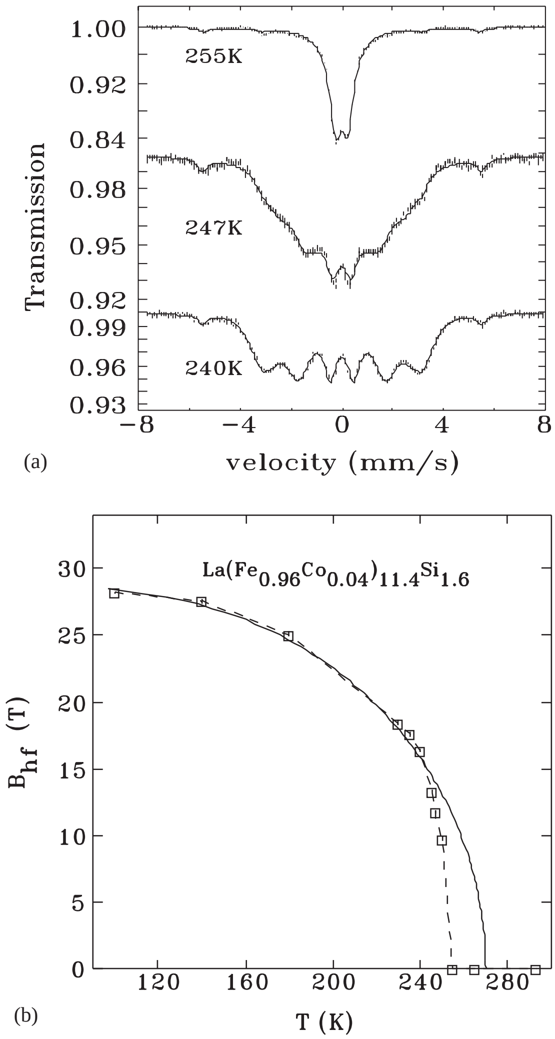
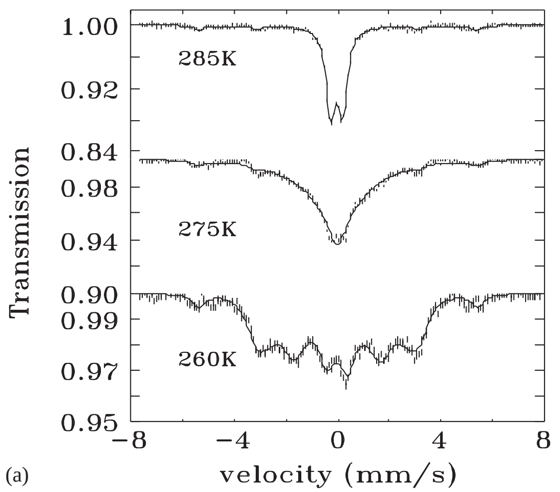


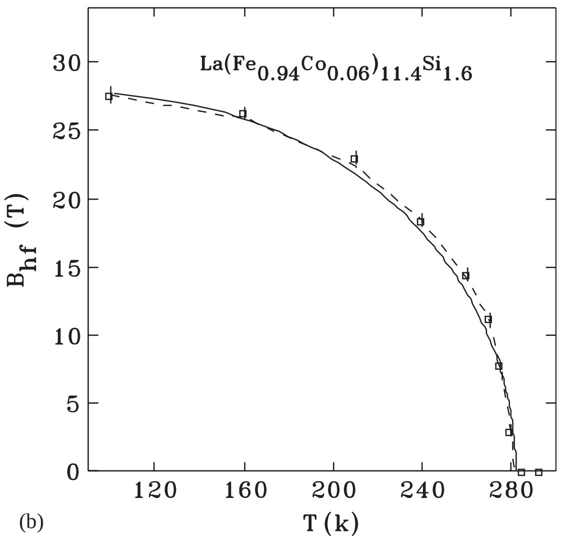
Fig. 6. (a) [57]Mössbauer spectra of $La(Fe_{0.96}Co_{0.04})_{11.4}Si_{1.6}$ at several temperatures. The solid lines are least-squares fits to the Mössbauer spectra; (b) temperature dependence of the average hyperfine magnetic field. The solid line is calculated using Brillouin function. The dashed line through the experimental data points is a guide to the eye.

change slowly as the magnetic pattern collapses gradually with increasing temperature into an asymmetric doublet characteristic of a paramagnetic state at T_c (Figs. 6(a) and 7(a)). The average hyperfine field B_{hf} decreases monotonically to zero with increasing temperature. There is no sign of the coexistence of the magnetic sextet and paramagnetic doublet.

The reduced hyperfine field for a ferromagnetic material, $b_{hf} = B_{hf}(T)/B_{hf}(0)$, can generally be described by a Brillouin function. The results of such fits for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ with $x = 0$, 0.04 and 0.06 are shown in Figs. 5(b), 6(b) and 7(b), respectively. The fitted T_c^{Br} values are listed in Table 1 together with the $T_c^{B_{hf}}$ values determined from the point at which $B_{hf}(T)$ goes to zero.



(a)



(b)

Fig. 7. (a) ^{57}Mössbauer spectra of $La(Fe_{0.94}Co_{0.06})_{11.4}Si_{1.6}$ at several temperatures. The solid lines are least-squares fits to the Mössbauer spectra; (b) temperature dependence of the average hyperfine magnetic field. The solid line is calculated using Brillouin function. The dashed line through the experimental data points is a guide to the eye.

Transition temperatures, T_c^{χ}, obtained from χ_{ac} measurements are identical, within error, to $T_c^{B_{hf}}$. However, for the alloys with $x=0$ and 0.04, $B_{hf}(T)$ changes more sharply than that predicted by the Brillouin function near T_c and so $T_c^{B_{hf}}$ is smaller than T_c^{Br}. Both DC magnetic measurements and the temperature dependence of Landau coefficients clearly indicate a second-order magnetic transition at T_c for $La(Fe_{0.96}Co_{0.04})_{11.4}Si_{1.6}$, however, the magnetic transition may be considered weakly first order as the temperature dependence of $B_{hf}(T)$ deviates from Brillouin function near T_c. This effect is small, the difference between $T_c^{B_{hf}}$ and T_c^{Br} for $LaFe_{11.4}Si_{1.6}$ is about three times that of $La(Fe_{0.96}Co_{0.04})_{11.4}Si_{1.6}$. The temperature dependence of $B_{hf}(T)$ for $La(Fe_{0.94}Co_{0.06})_{11.4}Si_{1.6}$ can be well fitted by Brillouin function near T_c which indicated a second-order magnetic transition.

4. Conclusions

Magnetization measurements and Mössbauer investigation indicate the occurrence of a strongly first-order transition between ferromagnetic and paramagnetic states at T_c in zero external field and a metamagnetic transition from paramagnetic to ferromagnetic state (P–F) above T_c for $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ with $x \leqslant 0.02$. However, the F–P magnetic transition at T_c is second order with no sign of metamagnetic transition above T_c for $x \geqslant 0.06$. It is interesting that the alloy with $x = 0.04$ shows a very weakly first-order magnetic transition at T_c in zero external field according to Mössbauer results, but no sign of metamagnetic transition above T_c from the DC measurement with a maximum applied field of 7 T. With increasing Co content, the magnetic transition (F–P) in $La(Fe_{1-x}Co_x)_{11.4}Si_{1.6}$ at T_c changes from a strongly first-order one to a weakly first-order one and eventually to a second-order transition. The temperature dependence of the mean hyperfine field for $LaFe_{11.4}Si_{1.6}$ is very sharp near T_c and strongly deviates from the Brillouin function which accounts for its large magnetic entropy change.

References

[1] V.K. Pecharsky, K.A. Gschneidner, Appl. Phys. Lett. 70 (1997) 3299.

[2] Hu Feng-xia, Bao-gen Shen, Ji-rong Sun, Zhao-hua Cheng, Guang-hui Rao, Xi-xiang Zhang, Appl. Phys. Lett. 78 (2001) 3675.

[3] Hu Feng-xia, Bao-gen Shen, Ji-rong Sun, Guan-jun Wang, Zhao-hua Cheng, Appl. Phys. Lett. 80 (2002) 3826.
[4] A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, T. Goto, Phys. Rev. B 65 (2002) 014410.
[5] X.B. Liu, Z. Altounian, J. Magn. Magn. Mater. 264 (2003) 209.
[6] M. Shimizu, Rep. Prog. Phys. 44 (1981) 329.
[7] M.J. Shimizu, Physique 43 (1982) 155.
[8] E. Gratz, A.S. Markosyan, J. Phys.: Condens. Matter 13 (2001) R385.
[9] A. Fujita, S. Fujieda, K. Fukamichi, J. Appl. Phys. 85 (1999) 4756.